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RESEARCH ARTICLE

Long-term influence of maize stover and its derived biochar on soil structure and organo-mineral complexes in Northeast China

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Abstract

The influence of biochar on the soil structure and aggregate stability has been debated in previous studies. To probe the action of biochar on soil aggregates, a 5-year field experiment was implemented in the brown earth soil of northeastern China. We determined the aggregate distribution (> 2000 μm, 250–2000 μm, 53–250 μm, and < 53 μm) and organic carbon (OC) and organo-mineral complex contents both in the topsoil (0–20 cm) and within the soil aggregates. Three treatments were studied as follows: control (basal application of mineral NPK fertilizer), biochar (biochar applied at a rate of 2.625 t ha^{-1}), and stover (maize stover applied at a rate of 7.5 t ha^{-1}), and all treatments received the same fertilization. The biochar and stover applications decreased the soil bulk and particle densities significantly ($p < 0.05$) and enhanced the soil total porosity. Both amendments significantly ($p < 0.05$) enhanced the total OC, heavy OC fractions, and organo-mineral complex quantities in the bulk soil as well as in all the studied aggregate fractions. Biochar and stover applications promoted the formation of small macroaggregates. A greater amount of organic matter was contained in the macroaggregates, which led to the formation of more organo-mineral complexes, thereby improving soil aggregate stability. However, the different mechanisms underlying the effect of biochar and stover on organo-mineral complexes need further research. Biochar and stover applications are both effective methods of improving the soil structure in Northeast China.

Keywords Biochar · Soil aggregates · Organo-mineral complexes · Soil structure · Carbon sequestration

Introduction

Soil structure plays a crucial function in soil physical, chemical, and biological processes (Peng et al. 2015). Soil structure can influence plant growth and change the soil organic carbon (SOC) content, regulate water transport, promote nutrient retention, and also provide habitats for biota; therefore, it is an important property affecting soil fertility and quality (Peng et al. 2015). Soil aggregates represent the base elements of soil structure, and the composition and distribution of these aggregates are important indicators of soil structure (Baiamonte et al. 2019; Six et al. 2000b). Soil aggregates could provide physical protection for SOC, which plays a binding agent role and is a vital substance in the aggregation process. The organic carbon (OC) contained in soil is approximately 3.3 times that contained in the atmospheric carbon pool (Lal 2004), and nearly 90% of the SOC is located in soil aggregates in the topsoil (Jastrow 1996). Organo-mineral complexes and soil aggregates have been shown to represent potential mechanisms underlying long-term carbon storage in

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soil (Huang et al. 2019; Weng et al. 2017). Soil organic matter stabilization occurs through several mechanisms, e.g., enclosing by mineral surfaces, insetting into layered mineral crystalline sheets, hydrophobic bonding, cation bridging, anion exchange, ligand exchange, Coulombic attraction, and van der Waals attraction (Bai et al. 2017; Sokol et al. 2019). Nevertheless, heightening SOC content and thus improving the forming of organo-mineral complexes and soil aggregates are an effective step for enhancing soil quality (Zhang et al. 2015).

The most popular practice of crop residue management in Northeast China is to burn them in the field. This practice produces large amounts of ash and smoke, which pollute the environment. An alternative environmentally friendly management approach can be turning crop straw into biochar and returning the product to soils to improve the SOC content. Biochar is the carbon-rich solid product of waste biomass pyrolysis performed in an anoxic environment (Chen et al. 2019b; Lehmann et al. 2011). Biochar can be used as a soil conditioner to enhance carbon sequestration (Li et al. 2018) and lessen greenhouse gas emissions (Lu et al. 2019); it has also been shown to dilute the bioavailabilities of heavy metals (Chen et al. 2019a; Xia et al. 2019; Yang et al. 2017) and organic contaminants (He et al. 2018; Qin et al. 2018) and improve the soil nutrient supply (Li et al. 2019), thereby increasing crop yields and quality (Nie et al. 2018). Biochar also increases the cation exchange capacity (CEC) (Wu et al. 2012) and pH (Chen et al. 2019b) of soils, and it improves soil enzymatic and microbial activities (Palansooriya et al. 2019), in turn promoting crop growth. Biochar as an amendment is known to enhance soil structure by increasing aggregate stability (Wang et al. 2017). However, these findings are inconclusive because some reports have suggested that biochar has no effect or a negative effect on soil aggregates (Borchard et al. 2014; Rahman et al. 2017). These inconsistent phenomena are related to different crop residue feedstocks, soil types and environments. Specially, the influence of maize stover and its biochar among different SOC fractions in differently sized soil aggregates remains largely unknown.

SOC can be classified as light fraction organic carbon (LFOC) and heavy fraction organic carbon (HFOC) based on its density. The LFOC is free OC, an important component of labile OC, and is mainly derived from crop residues and decaying animal bodies (Christensen 2010). The LFOC is not stored for long periods of time because it is easily degraded. The HFOC exists in the form of organo-mineral complexes, which are not easily degraded and are thus more stable than LFOC. The HFOC portion can occupy up to 91% of the total SOC (Kleber et al. 2015). It can therefore be assumed that different organic material inputs could have different effects on the production of organo-mineral complexes in the field (Li and Wu 2012).

Brown earth is the main soil type in Liaoning Province of China (Gao et al. 2018). This area is situated at one of the three golden maize (*Zea mays L*) belts of the world and is the major cereal cultivating area in China (Yang et al. 2017a`). Historically, little organic amendments have been utilized to the brown earth soil in this region. Although biochar as a soil conditioner has considerable benefits, there have been few studies on the effect of biochar on soil structure in the brown earth region. The effects of biochar on the organo-mineral complexes in this soil have never been studied. Therefore, we designed a long-term field experiment (5 years) involving maize stover and stover-derived biochar incorporation to assess the soil aggregates and organo-mineral complexes. The purpose of this study was to survey the long-term influences of maize stover and its biochar on (1) soil bulk density (BD), particle density (PD), and soil total porosity (TP); (2) soil water-stable aggregates and their stability; (3) SOC and soil organo-mineral complexes; and (4) the SOC and organo-mineral complexes within differently sized aggregates.

Materials and methods

Experimental site

A 5-year field experiment was implemented from May 2013 to October 2017 at a long-term field station of the Liaoning Biochar Engineering and Technology Research Center, Shenyang Agricultural University (41°49′N, 123°33′E). The location receives approximately 705 mm of annual precipitation. The average minimum and maximum temperatures were − 25 and 35.3 °C during the experimental period. This region is situated in Northeast China, Liaoning Province. The experimental site has a warm, semi-humid climate. The soil type in this region is brown earth, and the soil is classified as a Hapli-Udic Cambisol according to the Food and Agriculture Organization (FAO) classification system (An et al. 2015; Yang et al. 2017a). The frost-free period is approximately 150 days, while the entire growth period is 130~150 days. The annual precipitation during the entire growth period is 547 mm, and the average temperature is 20.7 °C (Lan et al. 2015). The type of agriculture in Liaoning Province is dry land rain-fed agriculture. The fundamental characteristics of the topsoil (0–20 cm) before the experiment are presented in Table s1. During the past 5 years, spring maize was continuously grown at this site with one harvest per year. The mineral fertilizers applied annually contained urea (120 kg N ha^{-1}), calcium superphosphate (60 kg P_2O_5 ha^{-1}), and potassium sulfate (60 kg K_2O ha^{-1}). All fertilizers were applied once before sowing the seeds.

Maize stover and biochar

Maize stover was gathered from the experimental field, then chopped into sections with a length of 50~70 mm. The maize stover biochar used in this experiment was supplied by Jinhefu Agriculture Development Company, Liaoning, China. The biochar was produced in a vertical kiln at 350–550 °C for 90 min. The properties of the maize stover and maize stover biochar are listed in Table s1.

Experimental design

The field experiment included three treatments: control (no amendments), biochar (biochar applied at a rate of 2.625 t ha^{-1}), and stover (maize stover applied at a rate of 7.5 t ha^{-1}). Regarding the carbon content, the applied amount of maize stover was almost equal to the stover biomass per year per hectare, and the biochar dosage was decided based on 35% productivity in the kiln after pyrolysis. Maize stover pieces and biochar powder (passed through a 2-mm sieve) were applied annually on the soil surface by hand before conducting rotary tillage of the plots. Spring maize was seeded in May and gathered at the end of September each year. The seeding rate was approximately 60,000 plants per hectare. A randomized block design with three replicates was used in the field experiment, and each plot had an area of 3.6 m × 10 m.

Soil sample preparation and analysis

After five growing seasons, in October 2017, topsoil (0–20 cm) samples were collected. Undisturbed soil samples (0–20 cm) were used to analyze soil aggregates collected in each plot, and the undisturbed soils were collected by a profile method (dig a profile, cut the undisturbed soil to a vertical depth of 20 cm, and then hold the samples in aluminum boxes). Subsamples were collected from five randomly selected locations in all plots and then mixed to make one complex sample. The undisturbed soils were brought to the laboratory and air-dried during which visible stones and plant debris were removed. Then, soils were then passed through an 8-mm sieve. The wet-sieving method was used to evaluate the soil aggregate content (Elliott 1986). Briefly, 50 g of air-dried soil was submersed in distilled water for 5 min on the top screen of the nested sieves. The sizes of the sieves were 2000 μm, 250 μm, and 53 μm. Four aggregate size fractions were acquired: large macroaggregates (> 2000 μm), small macroaggregates (250–2000 μm), microaggregates (53–250 μm), and the silt and clay fraction (< 53 μm). The sieves were shifted up and down by approximately 3 cm for 15 min, with approximately 20 strokes min^{-1}. The aggregate fractions remaining on each sieve were washed into aluminum boxes, oven-dried at 60 °C for 48 h, weighed, and placed in plastic bags. The soil BD was measured by the soil core and cutting ring method (Luo et al. 2016). The liquid pycnometer method was used to analyze PD (Walia and Dick 2018). The soil was air-dried in the laboratory, then sieved through 2-mm and 1-mm sieves. Subsamples were also sieved through a 0.15-mm mesh to determine the SOC contents by an elemental analyzer (Elementar Macro Cube, Langenselbold, Germany). The soil organic fractions were determined by the relative density method (Fu et al. 1983). Briefly, 5 g of air-dried soil (< 1 mm) was placed aside in a 100-ml centrifuge tube of known weight with 25 ml of sodium iodide aqueous solution (1.7 g cm^{-3}). After shaking the mixture for 1 h and centrifuging at 3000 rpm for 10 min, the supernatant was filtered and the floating material was washed with deionized water. The sodium iodide solution was collected for recycling. The procedure was repeated twice. The leftover contents in the centrifuge tubes, which consisted of the heavy fraction, were washed twice with deionized water, oven-dried at 40 °C, weighed, and kept in plastic bags for further analysis. The SOC content in the heavy fraction was determined by an elemental analyzer as mentioned earlier.

Calculation and statistical analysis

The soil aggregate content was determined as follows:

$$R_{\mathrm{i}} = \frac{W_i}{50} \tag{1}$$

where R_{i} represents the soil aggregate fraction (%) and W_i is the weight of each soil aggregate fraction (g).

The stability of soil aggregates has traditionally been assessed by calculating the mean weight diameter (MWD), geometric mean diameter (GMD), macroaggregate content ($R_{>250}$), and fractal dimension (D). The formulae for these parameters are as follows:

$$\mathrm{MWD} = \frac{\sum_{i=1}^{n} \overline{X}_i W_i}{\sum_{i=1}^{n} W_i} \tag{2}$$

$$\mathrm{GMD} = \mathrm{EXP}\left[\frac{\sum_{i=1}^{n} W_i \ln \overline{x}}{\sum_{i=1}^{n} W_i}\right] \tag{3}$$

$$R_{>250} = \frac{M_{>250}}{50} \tag{4}$$

$$\frac{\mathrm{M}_{(\mathrm{r}<\mathrm{x_i})}}{20} = \left[\frac{x_i}{x_{\max}}\right]^{3-\mathrm{D}} \tag{5}$$

where x_i is the mean diameter of every soil aggregate size (mm), w_i is the weight percentage of every soil aggregate size (%), and $M_{>250}$ is the weight of the macroaggregates (g).

Total porosity (TP) was calculated as follows:

$$\text{Total porosity} = \left(1 - \frac{\mathrm{BD}}{\mathrm{PD}}\right) \times 100\% \tag{6}$$

where BD refers to soil bulk density and PD refers to the soil particle density.

The soil organo-mineral complex index was calculated following Fu et al. (1983):

$$QC = \frac{HC \times Hm}{m} \times 100\% \tag{7}$$

$$DC = \frac{HC \times Hm}{SOC \times m} \times 100\% \tag{8}$$

$$QAC = MQ - SQ \tag{9}$$

$$DAC = \frac{MQ - SQ}{MC - SC} \tag{10}$$

where HC is the heavy SOC (%), Hm is the content of the heavy fraction (g), m is the weight of the sample (g), QC refers to the quantity of organo-mineral complexes in the soil (%), DC is the degree of organo-mineral complexes (%), QAC refers to the quantity of additional complexes (%), DAC refers to the degree of additional complexes (%), MQ represents the quantity of QCs under the biochar and stover treatments (%), SQ represents the quantity of QCs under the control treatment (%), MC refers to the SOC under the biochar and stover treatments (%), and SC refers to the SOC under the control treatment (%).

The relative contribution of SOC within different aggregate fractions was calculated as follows:

$$\text{Relative contribution} = \frac{\text{SOC within aggregate} \times \text{Aggregate content } (\%)}{\text{SOC}} \tag{11}$$

All data gathered in this research are presented as the mean ± standard deviation. We used one-way analysis of variance (ANOVA) to test the differences in soil parameters among the treatments. The least significant difference (LSD) method was also used to test for differences among treatments ($p < 0.05$).

Results

Soil bulk density, particle density, and total porosity

In this 5-year experiment, biochar and maize stover treatments both decreased the BD significantly ($P < 0.05$), and compared to the control, the BD decreased by 4.6 and 6.1% in the biochar and stover treatments, respectively (Table 1). The PD also changed. Biochar and stover decreased the PD significantly ($p < 0.05$) compared with the control, although their effects were not significantly different between the amendment treatments (Table 1). Although biochar decreased the BD and PD, the TP did not vary after the 5-year experiment; conversely, stover increased the TP significantly after the experimental period (Table 1).

Table 1 Effect of maize stover and its biochar on soil bulk density, particle density and total porosity

Treatment	BD (g cm^{-3})	PD (g cm^{-3})	TP (%)
Control	1.31 ± 0.01a	2.55 ± 0.01a	48.63 ± 0.41b
Biochar	1.25 ± 0.01b	2.48 ± 0.01b	49.53 ± 0.42b
Stover	1.23 ± 0.01b	2.49 ± 0.01b	50.60 ± 0.42a

BD bulk density, *PD* particle density, *TP* total porosity

Distinct lowercase letters indicate significant differences ($p < 0.05$) among the treatments in each column

Soil aggregates and their stability

Biochar and maize stover affected the water-stable aggregate composition and soil aggregate stability (Fig. 1, Table 2). No remarkable differences were observed in the large macroaggregate (> 2000 μm) fraction among the treatments. Compared to the control, biochar and stover improved the 250–2000 μm fraction by 14.91 and 55.69%, respectively. However, the microaggregate fraction was the smallest under the stover treatment and not significantly different between the control and biochar treatments. Finally, the silt and clay fractions (< 53 μm) in the treatments exhibited the following order: control > biochar = stover, indicating that biochar and stover both increased the large macroaggregates, and the effect of stover was stronger than that of biochar.

The MWD was not significantly different among the treatments after the 5-year experiment, and the values changed from 1.60 to 1.70 mm (Table 2). The GMD in the treatments exhibited the following order: stover = biochar > control treatments, and that under biochar and stover treatments was 23.91 and 37.72% higher than that under the control, respectively, indicating that biochar and stover increased soil aggregate stability. Biochar and stover treatments both increased the $R_{>250\mu m}$ values (macroaggregates), with the following order of $R_{>250\mu m}$ values: stover > biochar > control, and the values under the biochar and stover treatments were 7.98 and 22.52% higher than those of the control, respectively (Table 2). The D values exhibited a different trend from the other data, with an order of control > biochar > stover (Table 2). The order showed that organic input decreased the *D* value and that stover had a stronger impact on soil structure than biochar.

Soil organic carbon, heavy fraction organic carbon, and organo-mineral complexes

The SOC content was noticeably affected by biochar and maize stover applied as a soil amendment after five consecutive growing seasons. The SOC content increased by 24.21 and 34.49% under biochar and stover treatments, respectively

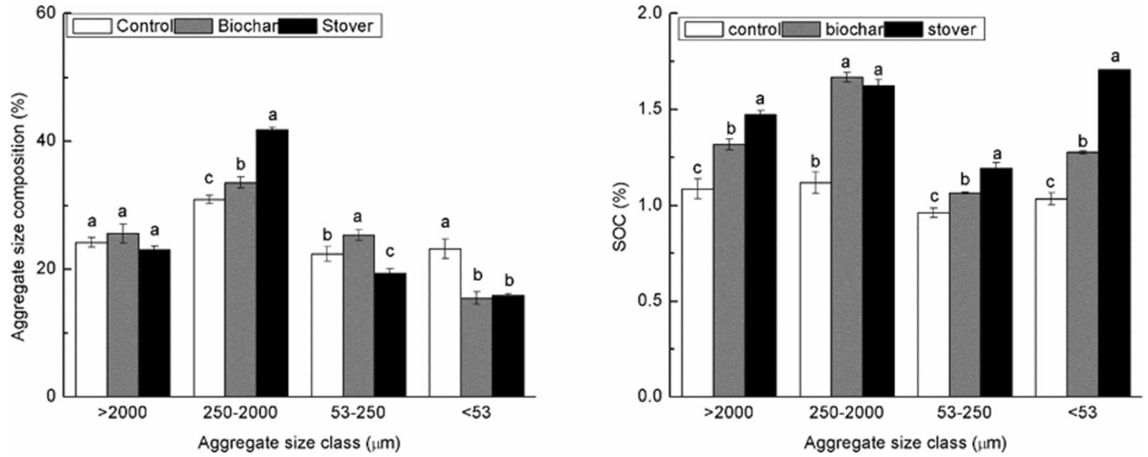

Fig. 1 Effect of maize stover and its biochar on soil water-stable aggregates and organic carbon within soil aggregates. Distinct lowercase letters indicate differences ($p < 0.05$) among the treatments in one aggregate size class

(Table 3). The HFOC showed a trend similar to that of the SOC (stover > biochar > control), being 20.77 and 40.11% higher under the biochar and stover treatments than under the control, respectively (Table 3). Biochar and stover improved the QC by 19.45 and 40.42%, respectively (Table 3). The DC in the biochar treatment was the lowest, and that in the stover treatment was the highest. The QAC increased with increasing SOC concentration. The DAC had the same tendency as the QAC in the biochar and stover treatments; the QAC under the stover treatment was approximately two times that under the biochar treatment, and the DAC was significantly greater under the stover treatment than under the biochar treatment (Table 3).

SOC content and organo-mineral complexes within aggregate fractions

The distribution of SOC associated with water-stable aggregates was significantly impacted by the biochar and stover treatments (Fig. 1). Biochar and stover both significantly enhanced the SOC content in differently sized aggregates ($p < 0.05$). The SOC within large macroaggregates (> 2000 μm) increased by 21.22 and 35.68% in the biochar and stover treatments, respectively, and that within small macroaggregates increased by 49.19 and 45.13%, respectively. The microaggregate fraction had the lowest SOC content of all aggregate sizes, with a 10.82 and 23.88% higher SOC under the biochar and stover treatments than under the control, respectively. The silt and clay fraction in the stover treatment had the highest SOC content, and the SOC concentration was improved by 64.99% compared to that of the control. In contrast, the SOC concentration of this fraction under biochar improved by only 23.40% compared to the control treatment.

Table 2 Effect of maize stover and its biochar on water-stable aggregate stability

Treatment	MWD (mm)	GMD (mm)	$R_{>250\ \mu m}$ (%)	D
Control	1.60 ± 0.04b	0.43 ± 0.04b	55.10 ± 1.27c	2.47 ± 0.04a
Biochar	1.70 ± 0.07a	0.56 ± 0.04a	59.14 ± 1.53b	2.40 ± 0.03b
Stover	1.66 ± 0.02ab	0.59 ± 0.01a	64.85 ± 0.69a	2.30 ± 0.01c

MWD mean weight diameter, *GMD* geometric mean diameter, $R_{>250\ \mu m}$ macroaggregate content, *D* fractal dimension

Distinct lowercase letters indicate differences ($p < 0.05$) among the treatments in one column

In general, the SOC contribution in the large macroaggregate fraction exhibited the following order: biochar = control > stover (Fig. 2). For the small macroaggregates, the SOC contribution rate was the highest under the stover treatment, followed by the control and biochar treatments. For the microaggregate fraction, the SOC contribution rate exhibited the following order: biochar = control > stover. Moreover, in the silt and clay fraction, the order was control > stover > biochar.

The HFOC concentration in each aggregate fraction had the same tendency as the HFOC in the bulk soil. These data might be explained by the increased organic material input in the aggregates. The QC in different aggregate fractions had the same tendency as the HFOC. These results show that biochar and stover additions both increased the QC in different aggregate fractions. The DC in the large macroaggregate fraction was not significantly different from that in other fractions, although the DC in the microaggregate fraction was the highest among all fractions. In each fraction, the QAC in the stover treatment was higher than that under the biochar treatment. The change in DAC differed among fractions; in the small macroaggregate fraction, the stover treatment had a higher DAC than the biochar treatment, and in the other

Table 3 Effect of maize stover and its biochar on soil organic carbon (SOC) content, heavy fraction organic carbon (HFOC) content, quantity of organo-mineral complexes (QC), degree of organo-mineral complexes (DC), quantity of additional complexes (QAC), and degree of additional complexes (DAC) in the bulk soil

Treatment	SOC (%)	HFOC (%)	QC (%)	DC (%)	QAC (%)	DAC (%)
Control	1.08 ± 0.11c	0.91 ± 0.12c	0.91 ± 0.12c	84.54 ± 1.15b	–	–
Biochar	1.34 ± 0.06b	1.09 ± 0.16b	1.09 ± 0.16b	81.30 ± 1.21c	0.18 ± 0.03b	67.91 ± 6.24a
Stover	1.45 ± 0.12a	1.28 ± 0.29a	1.28 ± 0.29a	88.26 ± 1.99a	0.37 ± 0.03a	99.06 ± 7.75b

All data are shown as the mean ± standard error ($n = 3$). Different lowercase letters in the same column indicate significant differences ($p < 0.05$). Distinct lowercase letters indicate differences ($p < 0.05$) among the treatments in one aggregate size class

fractions, the DAC had a stronger effect under the biochar treatment than the stover treatment (Table 4).

Discussion

Effect of maize stover and biochar on bulk density and total porosity

In previous studies, biochar and stover used as soil amendments both decreased the soil BD (Getahun et al. 2018; Li et al. 2018; Xu et al. 2018), and the results of our study corroborate those reports. Compared to the initial BD in 2013 (Table 1), the BD in the control showed no changes after 5-year field experiment, whereas the BD in the biochar and stover treatments decreased significantly. The effect of biochar and stover on BD might be explained by the decreased PD when the soil matrix was diluted by biochar and stover, which are lower density materials, and the increase in macropores between aggregates; thus, the different amendments to the soil also changed the PD (Pranagal et al. 2017). In this study, PD decreased significantly with the input of biochar and stover, although significant differences in PD were not observed between the biochar and stover treatments. Soil porosity is important for crops because of its immediate impact on soil aeration and root growth (Walia and Dick 2018). Biochar addition enhanced soil porosity in some previous studies (Obia et al. 2016), and biochar's effect on the soil TP mainly depends on the addition rate of biochar (Głąb et al. 2018). In the present study, biochar had no obvious effect on the TP, which might primarily be associated with the low application rate of biochar because the porosity of biochar was remarkably higher than that of stover before pyrolysis. Therefore, further investigations are still required to explore the effect of different biochar dosages on the TP in brown earth.

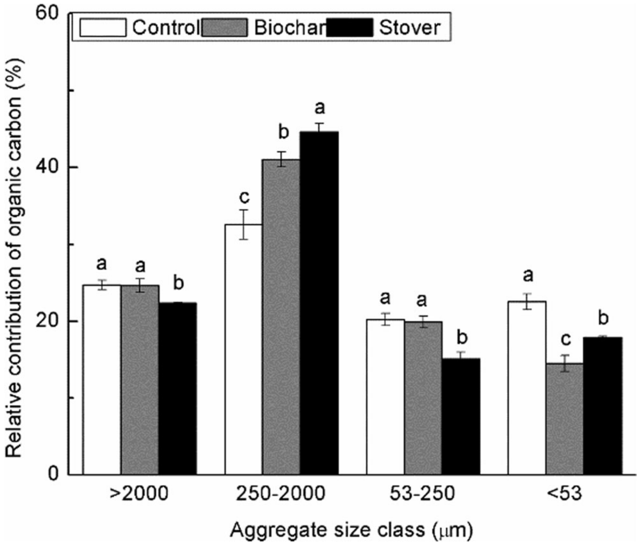

Fig. 2 Relative contributions of organic carbon in different aggregate fractions. The lowercase letters above columns indicate differences ($p < 0.05$) among the treatments within each aggregate size class

Effect of maize stover and biochar on soil aggregates and aggregate stability

Among the three treatments, biochar and stover application had a higher proportion of small macroaggregates and lower proportions of silt and clay fractions (Fig. 1); thus, our results demonstrate that the amendments enhanced the formation of macroaggregates after 5-year field experiments. Moreover, these amendments also improved the soil aggregate stability in the present study. The aggregate stability was reflected by the MWD, GMD, $R_{>250\ \mu m}$, and D value, with the MWD and GMD showing no remarkable differences between the biochar and stover treatments, which is an expected result because soil aggregate stability is a key indicator for soil erodibility (Six et al. 2000a). This phenomenon revealed that biochar and maize stover promoted the microaggregate fraction and silt and clay fraction to cluster into macroaggregates. Therefore, the $R_{>250\ \mu m}$ values were enhanced by the amendments in our study. However, the effect of biochar and stover had different effects on the soil aggregates in our study. Biochar application had a higher proportion of microaggregates than the control and stover treatments, while stover application had a higher proportion of the small macroaggregate fraction than the control and biochar treatments. These research findings are consistent with many previous studies (Du et al. 2016; Zhang et al. 2017); however, the mechanisms are not well understood. Several potential mechanisms might explain the

Table 4 Effect of maize stover and its biochar on heavy fraction organic carbon (HFOC) content, quantity of organo-mineral complexes (QC), degree of organo-mineral complexes (DC), quantity of additional complexes (QAC), and degree of additional complexes (DAC) in different aggregate size fractions

Aggregate size (μm)	Treatment	HFOC (%)	QC (%)	DC (%)	QAC (%)	DAC (%)
> 2000	Control	0.82 ± 0.47c	0.82 ± 0.05c	75.61 ± 4.29a	–	–
	Biochar	0.94 ± 0.42b	0.94 ± 0.04b	71.15 ± 3.18a	0.15 ± 0.04b	64.63 ± 9.02a
	Stover	1.03 ± 0.53a	1.03 ± 0.05a	69.81 ± 3.58a	0.21 ± 0.01a	52.99 ± 3.04b
250–2000	Control	0.87 ± 0.32c	0.87 ± 0.03c	78.08 ± 2.86a	–	–
	Biochar	1.01 ± 0.30b	1.01 ± 0.03b	60.73 ± 1.83c	0.14 ± 0.06b	25.46 ± 2.16b
	Stover	1.11 ± 0.09a	1.11 ± 0.01a	68.50 ± 0.56b	0.24 ± 0.04a	47.27 ± 7.83a
53–250	Control	0.81 ± 0.09c	0.81 ± 0.01c	83.86 ± 0.95b	–	–
	Biochar	0.92 ± 0.19b	0.92 ± 0.02b	86.77 ± 1.83a	0.12 ± 0.02b	113.65 ± 7.59a
	Stover	1.01 ± 0.15a	1.01 ± 0.02a	84.49 ± 1.29ab	0.20 ± 0.02a	87.09 ± 9.86b
< 53	Control	0.78 ± 0.13c	0.78 ± 0.01c	74.96 ± 1.22a	–	–
	Biochar	0.93 ± 0.12b	0.93 ± 0.01b	72.53 ± 0.98a	0.15 ± 0.01b	62.17 ± 3.04a
	Stover	1.03 ± 0.12a	1.03 ± 0.01a	60.10 ± 0.72b	0.25 ± 0.01a	37.25 ± 0.39b

different effects between biochar and maize stover on soil aggregates. First, most of the OC from maize stover is bioavailable OC, which can be easily used by microorganisms (Huang et al. 2018). Moreover, biochar is recalcitrant due to its chemical and biological stability (Singh et al. 2012). Second, the carbon input differs between these two amendments, with maize stover presenting higher carbon input than biochar in our study.

Effect of maize stover and its biochar on soil organic carbon, heavy fraction organic carbon, and organo-mineral complexes

Compared to the basic SOC content before the field experiment (Table s1), the SOC content hardly changed in the control treatment but increased significantly with the application of stover and biochar in our study (Table 3). The highest SOC content was discovered in the stover treatment because of the higher carbon input with the stover treatment compared with biochar (i.e., 3.22 t C ha^{-1} per year and 1.73 t C ha^{-1} per year, respectively). In a previous study that implemented equal total carbon inputs, the biochar application had a higher SOC content than the stover application due to the high stability of biochar carbon (Zhang et al. 2019). Although stover might have a relatively higher decomposition rate than biochar, the higher SOC content in stover could be related to the higher carbon input by stover. HFOC refers to the SOC fraction consisting of organo-mineral complexes, accounting for approximately 50~90% of SOC (Whalen et al. 2000). The highest HFOC concentration was found in the maize stover treatment (Table 3). Our study indicated that biochar and stover both promote the formation of organo-mineral complexes because the HFOC and QC both increased after the 5-year experiment. These results indicate that organic material inputs enhanced the QC, thereby promoting the formation of soil aggregates. Biochar decreased the DC and stover increased the DC in our study ($p < 0.05$), which might be related to the different compositions of biochar and stover. These results were likely associated with biochar's refractory structure and poor ability to physically interact with the mineral fraction compared to the stover amendment (Czimczik and Masiello 2007); moreover, the biochar carbon stability could have affected the DC, which mainly depends on the clay contents and mineral composition of the soils (Fang et al. 2018). However, the dynamics and mechanisms of biochar and mineral interactions in soils require further research (Singh et al. 2014). Chi et al. (2014) reported that the heavy fraction and QC increased under different long-term fertilization treatments, and DC decreased in the same way. These responses depended primarily on the composition of organic material inputs and are stronger with increased stover input (Gao et al. 2017a). The QAC and DAC could reflect differences of soil fertility. In this study, stover and biochar both improved the soil fertility after five-year field experiments. This study indicated that enhancing SOC can boost the formation of organo-mineral complexes and then promote soil aggregation.

SOC content and organo-mineral complexes within soil aggregate fractions

Soil macroaggregates and microaggregates impact the process of soil carbon sequestration (Singh et al. 2019; Six et al. 2004). SOC within soil aggregates has been regarded as a stable carbon sink in recent studies, and the formation and stability of aggregate are connected to soil C dynamics (Gao et al. 2017b). In this study, biochar application generated to increase the SOC content within different aggregate fractions, especially in macroaggregates fractions (> 250 μm), and the relative contributions of organic carbon in macroaggregates were higher than those of microaggregate, silt, and clay fractions, indicating that biochar carbon could be well protected by macroaggregates and benefited SOC sequestration (Liu et al. 2014). Almost all the size fractions in the stover treatment had higher OC concentrations than those in the biochar treatment because of more exogenous carbon input through the stover (Yang et al. 2017a). These data further indicate that organic material input increased carbon sequestration in macroaggregates significantly, similar to the results reported in previous studies (Du et al. 2016). This phenomenon indicates that biochar and stover amendments can both increase the macroaggregate content, thus further promoting the stability of SOC. Macroaggregates can protect SOC from microbial degradation and thus retain OC in soil for a long time (Grunwald et al. 2016). In addition, the influence of biochar on soil carbon sequestration not only depends on its stable properties but also its contribution towards soil aggregates. The order of the HFOC in the aggregate fractions was as follows: stover > biochar > control. These results indicate that organic matter addition enhanced OC in the soil, in turn improving the QC and increasing the macroaggregate content. In the present study, biochar and stover applications both increased the SOC and QC. The QC increased in all aggregate fractions with organic material input. This result indicates that organic carbon inputs are stabilized with mineral particles in long-term experiments. Moreover, the different composition of organic inputs might have different mechanisms between carbon and minerals. Therefore, the mechanisms between biochar and stover on the formation of organo-mineral complexes remain unclear. A lower DC in macroaggregates indicates that coarser OC is enclosed within the macroaggregates (Fu et al. 1983). In our study, the DC showed a different trend in different aggregate fractions, with a lower DC indicating that coarser OC was protected in the small macroaggregate fraction. This result also indicated that the amendments had a positive effect on SOC via macroaggregates. Compared to the biochar amendment, the stover treatment had a higher QAC in all aggregate fractions; however, biochar had a stronger effect on the DAC in the large macroaggregate, microaggregate, and silt and clay fractions than the stover treatment. This result suggests that the organic amendments improved soil aggregation and enhanced the organo-mineral complexes after the 5-year experiment; however, the mechanisms require further research in the future.

Conclusions

The results of this long-term field study (5 years) indicated that maize stover and its biochar application had significant effects on soil structure in Northeast China. Maize stover and its biochar affected the soil structure by increasing the soil macroaggregate content ($R_{>250\ \mu m}$) and soil aggregate stability (MWD, GMD) and decreasing the soil BD. However, differences were not observed in the aggregate stability between the biochar and stover treatments. In addition, the SOC and HFOC were also increased by the biochar and stover amendments. Biochar and stover application enhanced the SOC in macroaggregates and the relative contribution of organic carbon in small macroaggregates. These results demonstrate that the positive effect of biochar and stover on SOC occurs through soil aggregation. Both biochar and stover enhanced the QC to improve the macroaggregates contents, and the decreased DC under the biochar application may have been related to the stable characteristics of biochar. Our study demonstrated that organic amendments enhance the formation of macroaggregates by organo-mineral complexes, which might protect the SOC. Additional research is required on the different mechanisms between biochar and stover on organo-mineral complexes. Biochar and stover applications are both effective methods of improving the soil structure.

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